CHAPTER 15

CHARACTERISTICS, APPLICATIONS, AND PROCESSING OF POLYMERS

PROBLEM SOLUTIONS

Stress-Strain Behavior

15.1 From Figure 15.3, the elastic modulus is the slope in the elastic linear region of the 20°C curve, which is

$$E = \frac{\Delta\,(\text{stress})}{\Delta\,(\text{strain})} = \frac{30 \text{ MPa} - 0 \text{ MPa}}{9 \text{ x } 10^{-3} - 0} = 3.3 \text{ GPa} \quad (483{,}000 \text{ psi})$$

The value range cited in Table 15.1 is 2.24 to 3.24 GPa (325,000 to 470,000 psi). Thus, the plotted value is a little on the high side.

The tensile strength corresponds to the stress at which the curve ends, which is 52 MPa (7500 psi). This value lies within the range cited in Table 15.1—48.3 to 72.4 MPa (7000 to 10,500 psi).

Viscoelastic Deformation

15.2 The explanation of viscoelasticity is given in Section 15.4.

15.3 This problem asks for a determination of the relaxation modulus of a viscoelastic material, which behavior is according to Equation 15.10--i.e.,

$$\sigma(t) = \sigma(0) \exp\left(-\frac{t}{\tau}\right)$$

We want to determine σ(10), but it is first necessary to compute τ from the data provided in the problem statement. Thus, solving for τ from the above expression,

$$\tau = \frac{-t}{\ln\left[\frac{\sigma(t)}{\sigma(0)}\right]} = \frac{-30 \text{ s}}{\ln\left[\frac{0.5 \text{ MPa}}{3.5 \text{ MPa}}\right]} = 15.4 \text{ s}$$

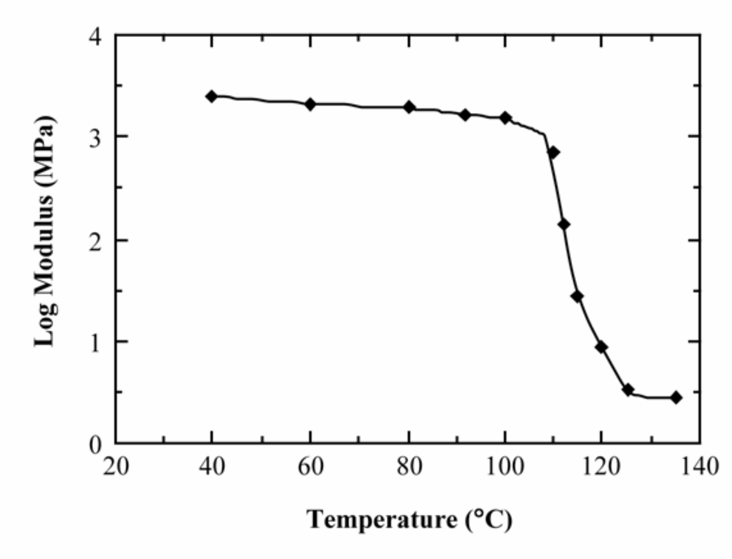
Therefore,

$$\sigma(10) = (3.5 \text{ MPa}) \exp\left(-\frac{10 \text{ s}}{15.4 \text{ s}}\right) = 1.83 \text{ MPa}$$

Now, using Equation 15.1

$$E_r(10) = \frac{\sigma(10)}{\varepsilon_0} = \frac{1.83 \text{ MPa}}{0.5} = 3.66 \text{ MPa} \quad (522 \text{ psi})$$

15.4 Below is plotted the logarithm of $E_r(10)$ versus temperature.



The glass-transition temperature is that temperature corresponding to the abrupt decrease in log $E_r(10)$, which for this PMMA material is about 115°C.

15.5 We are asked to make schematic strain-time plots for various polystyrene materials and at several temperatures.

(a) Crystalline polystyrene at 70°C behaves in a glassy manner (Figure 15.8, curve *A*); therefore, the strain-time behavior would be as Figure 15.5(b).

(b) Amorphous polystyrene at 180°C behaves as a viscous liquid (Figure 15.8, curve *C*); therefore, the strain-time behavior will be as Figure 15.5(d).

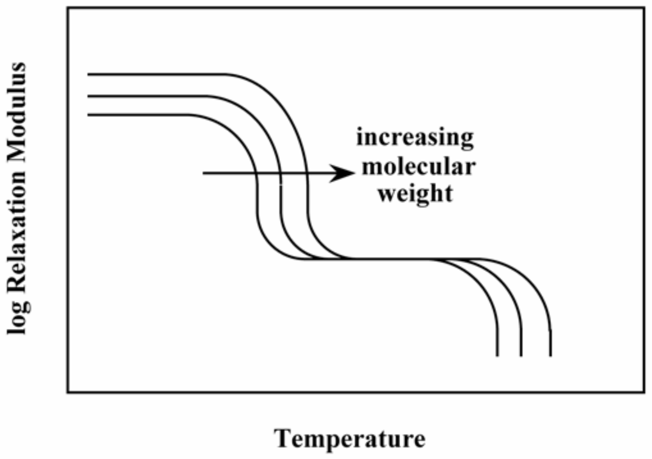
(c) Crosslinked polystyrene at 180°C behaves as a rubbery material (Figure 15.8, curve *B*); therefore, the strain-time behavior will be as Figure 15.5(c).

(d) Amorphous polystyrene at 100°C behaves as a leathery material (Figure 15.7); therefore, the strain-time behavior will be as Figure 15.5(c).

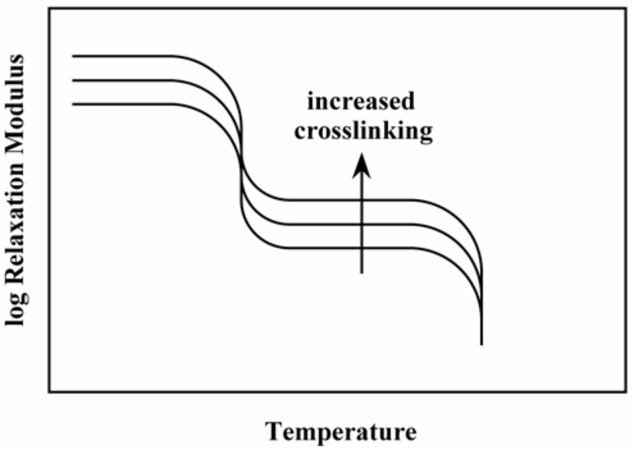
15.6 (a) Stress relaxation tests are conducted by rapidly straining the material elastically in tension, holding the strain level constant, and then measuring the stress as a function of time. For viscoelastic creep tests, a stress (usually tensile) is applied instantaneously and maintained constant while strain is measured as a function of time.

(b) The experimental parameters of interest from the stress relaxation and viscoelastic creep tests are the relaxation modulus and creep modulus (or creep compliance), respectively. The relaxation modulus is the ratio of stress measured after 10 s and strain (Equation 15.1); creep modulus is the ratio of stress and strain taken at a specific time (Equation 15.2).

15.7 (a) This portion of the problem calls for a plot of log $E_r(10)$ versus temperature demonstrating how the behavior changes with increased molecular weight. Such a plot is given below. Increasing molecular weight increases both glass-transition and melting temperatures.



(b) We are now called upon to make a plot of log $E_r(10)$ versus temperature demonstrating how the behavior changes with increased crosslinking. Such a plot is given below. Increasing the degree of crosslinking will increase the modulus in both glassy and rubbery regions.



Fracture of Polymers

Miscellaneous Mechanical Considerations

15.8 For thermoplastic polymers, five factors that favor brittle fracture are as follows: (1) a reduction in temperature, (2) an increase in strain rate, (3) the presence of a sharp notch, (4) increased specimen thickness, and (5) modifications of the polymer structure.

15.9 (a) The fatigue limits for PMMA and the steel alloy are 10 MPa (1450 psi) and 290 MPa (42,200 psi), respectively.

(b) At 10^6 cycles, the fatigue strengths for nylon 6 and 2014-T6 aluminum are 11 MPa (1600 psi) and 200 MPa (30,000 psi), respectively.

Deformation of Semicrystalline Polymers

15.10 (a) and (b) The mechanisms by which semicrystalline polymers elastically and plastically deform are described in Section 15.7.

(c) The explanation of the mechanism by which elastomers elastically deform is provided in Section 15.9.

Factors That Influence the Mechanical Properties of Semicrystalline Polymers

Deformation of Elastomers

15.11 (a) The tensile modulus is not directly influenced by a polymer's molecular weight.

(b) Tensile modulus increases with increasing degree of crystallinity for semicrystalline polymers. This is due to enhanced secondary interchain bonding which results from adjacent aligned chain segments as percent crystallinity increases. This enhanced interchain bonding inhibits relative interchain motion.

(c) Deformation by drawing also increases the tensile modulus. The reason for this is that drawing produces a highly oriented molecular structure, and a relatively high degree of interchain secondary bonding.

(d) When an undeformed semicrystalline polymer is annealed below its melting temperature, the tensile modulus increases.

(e) A drawn semicrystalline polymer that is annealed experiences a decrease in tensile modulus as a result of a reduction in chain-induced crystallinity, and a reduction in interchain bonding forces.

15.12 (a) The tensile strength of a semicrystalline polymer increases with increasing molecular weight. This effect is explained by increased chain entanglements at higher molecular weights.

(b) Increasing the degree of crystallinity of a semicrystalline polymer leads to an enhancement of the tensile strength. Again, this is due to enhanced interchain bonding and forces; in response to applied stresses, interchain motions are thus inhibited.

(c) Deformation by drawing increases the tensile strength of a semicrystalline polymer. This effect is due to the highly oriented chain structure that is produced by drawing, which gives rise to higher interchain secondary bonding forces.

(d) Annealing an undeformed semicrystalline polymer produces an increase in its tensile strength.

15.13 Normal butane has a higher melting temperature as a result of its molecular structure (Section 14.2). There is more of an opportunity for van der Waals bonds to form between two molecules in close proximity to one another than for isobutane because of the linear nature of each normal butane molecule.

15.14 This problem gives us the tensile strengths and associated number-average molecular weights for two poly(methyl methacrylate) materials and then asks that we estimate the tensile strength for $\overline{M}_n$ = 40,000 g/mol. Equation 15.3 cites the dependence of the tensile strength on $\overline{M}_n$. Thus, using the data provided in the problem statement, we may set up two simultaneous equations from which it is possible to solve for the two constants TS_∞ and A. These equations are as follows:

$$50 \text{ MPa} = TS_\infty - \frac{A}{30{,}000 \text{ g/mol}}$$

$$150 \text{ MPa} = TS_\infty - \frac{A}{50{,}000 \text{ g/mol}}$$

Thus, the values of the two constants are: TS_∞ = 300 MPa and A = 7.50 x 10^6 MPa-g/mol. Substituting these values into Equation 15.3 for $\overline{M}_n$ = 40,000 g/mol leads to

$$TS = TS_\infty - \frac{A}{40{,}000 \text{ g/mol}}$$

$$= 300 \text{ MPa} - \frac{7.50 \text{ x } 10^6 \text{ MPa - g/mol}}{40{,}000 \text{ g/mol}}$$

$$= 112.5 \text{ MPa}$$

15.15 This problem gives us the tensile strengths and associated number-average molecular weights for two polyethylene materials and then asks that we estimate the $\overline{M}_n$ that is required for a tensile strength of 140 MPa. Equation 15.3 cites the dependence of the tensile strength on $\overline{M}_n$. Thus, using the data provided in the problem statement, we may set up two simultaneous equations from which it is possible to solve for the two constants TS_∞ and A. These equations are as follows:

$$90 \text{ MPa} = TS_\infty - \frac{A}{20{,}000 \text{ g/mol}}$$

$$180 \text{ MPa} = TS_\infty - \frac{A}{40{,}000 \text{ g/mol}}$$

Thus, the values of the two constants are: TS_∞ = 270 MPa and A = 3.6 x 10^6 MPa-g/mol. Solving for $\overline{M}_n$ in Equation 15.3 and substituting TS = 140 MPa as well as the above values for TS_∞ and A leads to

$$\overline{M}_n = \frac{A}{TS_\infty - TS}$$

$$= \frac{3.6 \times 10^6 \text{ MPa - g/mol}}{270 \text{ MPa} - 140 \text{ MPa}} = 27{,}700 \text{ g/mol}$$

15.16 For each of four pairs of polymers, we are to do the following: (1) determine whether or not it is possible to decide which has the higher tensile modulus; (2) if so, note which has the higher tensile modulus and then state the reasons for this choice; and (3) if it is not possible to decide, then state why.

(a) Yes, it is possible. The linear and isotactic poly(vinyl chloride) will display a greater tensile modulus. Linear polymers are more likely to crystallize that branched ones. In addition, polymers having isotactic structures will normally have a higher degree of crystallinity that those having atactic structures. Increasing a polymer's crystallinity leads to an increase in its tensile modulus. In addition, tensile modulus is independent of molecular weight--the atactic/branched material has the higher molecular weight.

(b) Yes, it is possible. The block styrene-butadiene copolymer with 10% of possible sites crosslinked will have the higher modulus. Block copolymers normally have higher degrees of crystallinity than random copolymers of the same material. A higher degree of crystallinity favors larger moduli. In addition, the block copolymer also has a higher degree of crosslinking; increasing the amount of crosslinking also enhances the tensile modulus.

(c) No, it is not possible. Branched polyethylene will tend to have a low degree of crystallinity since branched polymers don't normally crystallize. The atactic polypropylene probably also has a relatively low degree of crystallinity; atactic structures also don't tend to crystallize, and polypropylene has a more complex repeat unit structure than does polyethylene. Tensile modulus increases with degree of crystallinity, and it is not possible to determine which polymer is more crystalline. Furthermore, tensile modulus is independent of molecular weight.

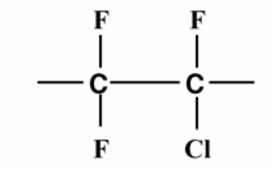
15.17 For each of four pairs of polymers, we are to do the following: (1) determine whether or not it is possible to decide which has the higher tensile strength; (2) if it is possible, then note which has the higher tensile strength and then state the reasons for this choice; and (3) if it is not possible to decide, to state why.

(a) Yes, it is possible. The linear and isotactic material will have the higher tensile strength. Both linearity and isotacticity favor a higher degree of crystallinity than do branching and atacticity; and tensile strength increases with increasing degree of crystallinity. Furthermore, the molecular weight of the linear/isotactic material is higher (100,000 g/mol versus 75,000 g/mol), and tensile strength increases with increasing molecular weight.

(b) No, it is not possible. Alternating copolymers tend to be more crystalline than graft copolymers, and tensile strength increases with degree of crystallinity. However, the graft material has a higher degree of crosslinking, and tensile strength increases with the percentage of crosslinks.

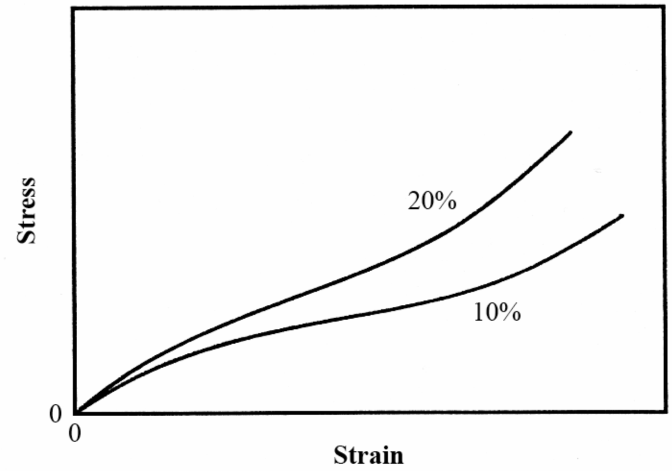
(c) Yes, it is possible. The network polyester will display a greater tensile strength. Relative chain motion is much more restricted than for the lightly branched polytetrafluoroethylene since there are many more of the strong covalent bonds for the network structure.

15.18 The strength of a polychlorotrifluoroethylene having the repeat unit structure

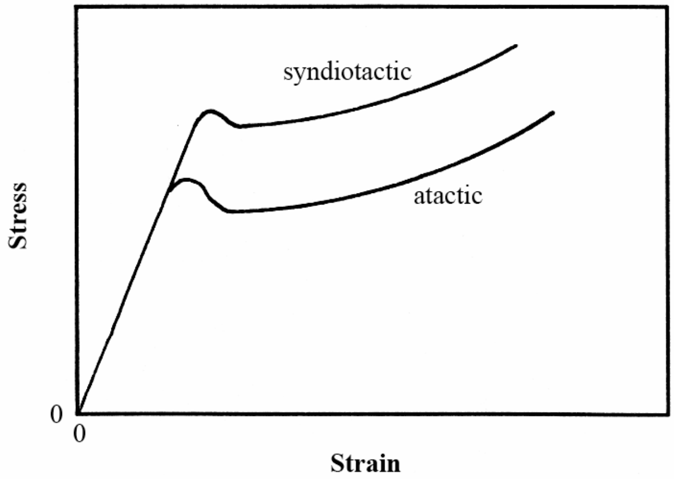


will be greater than for a polytetrafluoroethylene having the same molecular weight and degree of crystallinity. The replacement of one fluorine atom within the PTFE repeat unit with a chlorine atom leads to a higher interchain attraction, and, thus, a stronger polymer. Furthermore, poly(vinyl chloride) is stronger than polyethylene (Table 15.1) for the same reason.

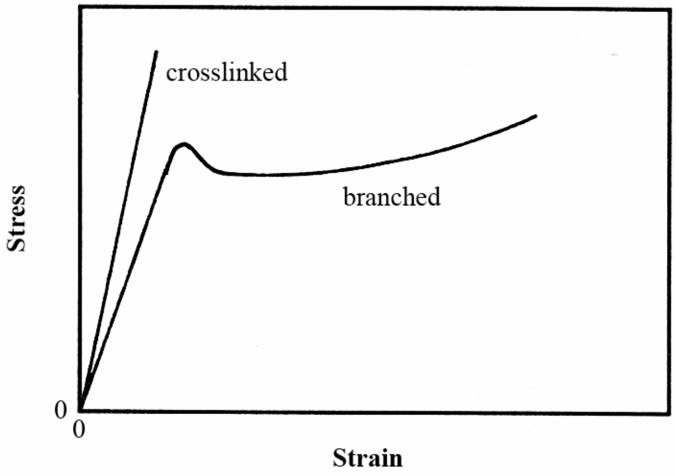
15.19 (a) Shown below are the stress-strain curves for the two polyisoprene materials, both of which have a molecular weight of 100,000 g/mol. These two materials are elastomers and will have curves similar to curve *C* in Figure 15.1. However, the curve for the material having the greater number of crosslinks (20%) will have a higher elastic modulus at all strains.



(b) Shown below are the stress-strain curves for the two polypropylene materials. These materials will most probably display the stress-strain behavior of a normal plastic, curve *B* in Figure 15.1. However, the syndiotactic polypropylene has a higher molecular weight and will also undoubtedly have a higher degree of crystallinity; therefore, it will have a higher strength.



(c) Shown below are the stress-strain curves for the two polyethylene materials. The branched polyethylene will display the behavior of a normal plastic, curve *B* in Figure 15.1. On the other hand, the heavily crosslinked polyethylene will be stiffer, stronger, and more brittle (curve *A* of Figure 15.1).



15.20 Two molecular characteristics essential for elastomers are: (1) they must be amorphous, having chains that are extensively coiled and kinked in the unstressed state; and (2) there must be some crosslinking.

15.21 This question asks us to choose from a list of materials those which would be expected to be elastomers and those which would be thermosetting polymers.

(a) Linear and crystalline polyethylene would be neither an elastomer nor a thermoset since it is a linear polymer.

(b) Phenol-formaldehyde having a network structure would be a thermosetting polymer since it has a network structure. It would not be an elastomer since it does not have a crosslinked chain structure.

(c) Heavily crosslinked polyisoprene having a glass transition temperature of 50°C would be a thermosetting polymer because it is heavily crosslinked. It would not be an elastomer since it is heavily crosslinked and room temperature is below its T_g.

(d) Lightly crosslinked polyisoprene having a glass transition temperature of –60°C is both an elastomer and a thermoset. It is an elastomer because it is lightly crosslinked and has a T_g below room temperature. It is a thermoset because it is crosslinked.

(e) Linear and partially amorphous poly(vinyl chloride) is neither an elastomer nor a thermoset. In order to be either it must have some crosslinking.

15.22 This problem asks that we compute the fraction of possible crosslink sites in 15 kg of polychloroprene when 5.2 kg of S is added, assuming that, on the average, 5.5 sulfur atoms participate in each crosslink bond. Given the butadiene repeat unit in Table 14.5, we may calculate its molecular weight as follows:

$$A(\text{chloroprene}) = 4(A_{\text{C}}) + 5(A_{\text{H}}) + A_{\text{Cl}}$$

$$= (4)(12.01 \text{ g/mol}) + 5(1.008 \text{ g/mol}) + 35.45 \text{ g/mol} = 88.53 \text{ g/mol}$$

Which means that in 15 kg of chloroprene there are $\dfrac{15{,}000 \text{ g}}{88.53 \text{ g/mol}} = 169.4 \text{ mol} = n_{\text{chloro}}$.

For the vulcanization of polychloroprene, there are two possible crosslink sites per repeat unit—one for each of the two carbon atoms that are doubly bonded. Furthermore, each of these crosslinks forms a bridge between two repeat units. Therefore, we can say that there is the equivalent of one crosslink per repeat unit. Let us now calculate the number of moles of sulfur (n_{sulfur}) that react with the chloroprene, by taking the mole ratio of sulfur to chloroprene, and then dividing this ratio by 5.5 atoms per crosslink; this yields the fraction of possible sites that are crosslinked. Thus

$$n_{\text{sulfur}} = \frac{5200 \text{ g}}{32.06 \text{ g/mol}} = 162.2 \text{ mol}$$

And

$$\text{fraction sites crosslinked} = \frac{\dfrac{n_{\text{sulfur}}}{n_{\text{chloro}}}}{5.5} = \frac{\dfrac{162.2 \text{ mol}}{169.4 \text{ mol}}}{5.5} = 0.174$$

15.23 For an alternating acrylonitrile-butadiene copolymer, we are asked to compute the weight percent sulfur necessary for complete crosslinking, assuming that, on the average, four sulfur atoms participate in each crosslink. The acrylonitrile and butadiene repeat units are shown in Table 14.5, from which it may be noted that there are two possible crosslink sites on each butadiene repeat unit (one site at each of the two carbon atoms that are doubly bonded), and no possible sites for acrylonitrile; also, since it is an alternating copolymer, the ratio of butadiene to acrylonitrile repeat units is 1:1. Thus, for each pair of combined butadiene-acrylonitrile repeat units which crosslink, eight sulfur atoms are required, or, for complete crosslinking, the sulfur-to-(acrylonitrile-butadiene) ratio is 4:1.

Now, let us consider as our basis, one mole of the combined acrylonitrile-butadiene repeat units. In order for complete crosslinking, four moles of sulfur are required. Thus, for us to convert this composition to weight percent, it is necessary to convert moles to mass. The acrylonitrile repeat unit consists of three carbon atoms, three hydrogen atoms, and one nitrogen atom; the butadiene repeat unit is composed of four carbons and six hydrogens. This gives a molecular weight for the combined repeat unit of

$$m(\text{acrylonitrile-butadiene}) = 3(A_C) + 3(A_H) + A_N + 4(A_C) + 6(A_H)$$

$$= 7(12.01\text{ g/mol}) + 9(1.008\text{ g/mol}) + 14.007\text{ g/mol} = 107.15\text{ g/mol}$$

Or, in one mole of this combined repeat unit, there are 107.15 g. Furthermore, for complete crosslinking 4.0 mol of sulfur is required, which amounts to (4.0 mol)(32.06 g/mol) = 128.24 g. Thus, the concentration of S in weight percent C_S (using Equation 4.3) is just

$$C_S = \frac{128.24\ \text{g}}{128.24\ \text{g} + 107.15\ \text{g}} \times 100 = 54.5\text{ wt\%}$$

15.24 This problem asks for us to determine how many crosslinks form per isoprene repeat unit when 45.3 wt% sulfur is added, assuming that, on the average, five sulfur atoms participate in each crosslink. If we arbitrarily consider 100 g of the vulcanized material, 45.3 g will be sulfur and 54.7 g will be polyisoprene. Next, let us find how many moles of sulfur and isoprene correspond to these masses. The atomic weight of sulfur is 32.06 g/mol, and thus,

$$\text{\# moles S} = \frac{45.3\ \text{g}}{32.06\ \text{g/mol}} = 1.41\ \text{mol}$$

Now, in each isoprene repeat unit there are five carbon atoms and eight hydrogen atoms. Thus, the molecular weight of a mole of isoprene units is

$$(5)(12.01\ \text{g/mol}) + (8)(1.008\ \text{g/mol}) = 68.11\ \text{g/mol}$$

Or, in 54.7 g of polyisoprene, the number of moles is equal to

$$\text{\# moles isoprene} = \frac{54.7\ \text{g}}{68.11\ \text{g/mol}} = 0.793\ \text{mol}$$

Therefore, the ratio of moles of S to the number of moles of polyisoprene is

$$\frac{1.41\ \text{mol}}{0.793\ \text{mol}} : 1 \ = \ 1.78 : 1$$

When all possible sites are crosslinked, the ratio of the number of moles of sulfur to the number of moles of isoprene is 5:1; this is because there are two crosslink sites per repeat unit and each crosslink is shared between repeat units on adjacent chains, and there are 5 sulfur atoms per crosslink. Finally, to determine the fraction of sites that are crosslinked, we just divide the actual crosslinked sulfur/isoprene ratio by the completely crosslinked ratio. Or,

$$\text{fraction of repeat unit sites crosslinked} = \frac{1.78/1}{5/1} \ = \ 0.356$$

15.25 We are asked what weight percent of sulfur must be added to polyisoprene in order to ensure that 10% of possible sites are crosslinked, assuming that, on the average, 3.5 sulfur atoms are associated with each crosslink. Table 14.5 shows the chemical repeat unit for isoprene. For each of these units there are two possible crosslink sites; one site is associated with each of the two carbon atoms that are involved in the chain double bond. Since 10% of the possible sites are crosslinked, for each 100 isoprene repeat units 10 of them are crosslinked; actually there are two crosslink sites per repeat unit, but each crosslink is shared by two chains. Furthermore, on the average we assume that each crosslink is composed of 3.5 sulfur atoms; thus, there must be 3.5 x 10 or 35 sulfur atoms added for every 100 isoprene repeat units. In terms of moles, it is necessary to add 35 moles of sulfur to 100 moles of isoprene. The atomic weight of sulfur is 32.06 g/mol, while the molecular weight of isoprene is

$$A(\text{isoprene}) = 5(A_\text{C}) + 8(A_\text{H})$$

$$= (5)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) = 68.11 \text{ g/mol}$$

The mass of sulfur added (m_S) is

$$m_\text{S} = (35 \text{ mol})(32.06 \text{ g/mol}) = 1122 \text{ g}$$

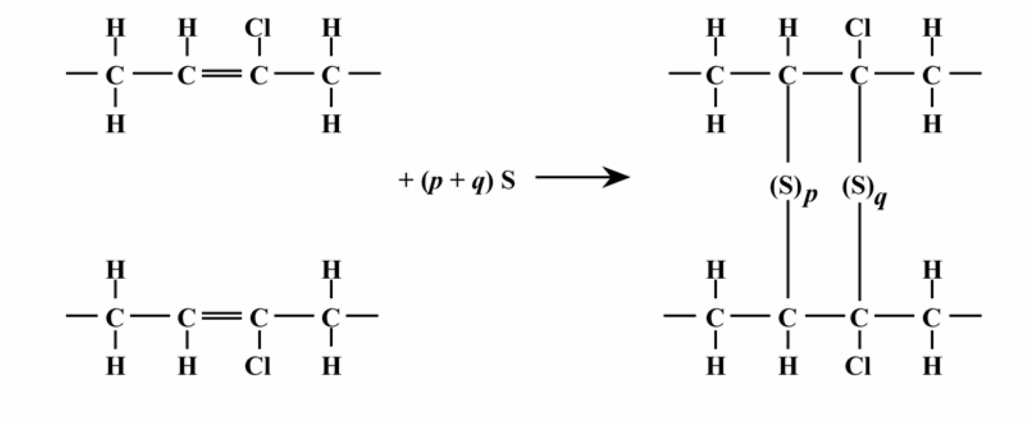
While for isoprene

$$m_\text{ip} = (100 \text{ mol})(68.11 \text{ g/mol}) = 6811 \text{ g}$$

Or, the concentration of sulfur in weight percent (Equation 4.3) is just

$$C_\text{S} = \frac{m_\text{S}}{m_\text{S} + m_\text{ip}} \times 100 = \frac{1122 \text{ g}}{1122 \text{ g} + 6811 \text{ g}} \times 100 = 14.1 \text{ wt\%}$$

15.26 The reaction by which a chloroprene rubber may become vulcanized is as follows:



Crystallization

15.27 In this problem we are asked to determine the values of the constants n and k (Equation 10.17) for the crystallization of polypropylene at 150°C (Figure 15.17). One way to solve this problem is to take two values of percent recrystallization (which is just 100y, Equation 10.17) and their corresponding time values, then set up two simultaneous equations, from which n and k may be determined. In order to expedite this process, we will rearrange and do some algebraic manipulation of Equation 10.17. First of all, we rearrange as follows:

$$1 - y = \exp\left(-kt^n\right)$$

Now taking natural logarithms

$$\ln (1 - y) = -kt^n$$

Or

$$-\ln (1 - y) = kt^n$$

which may also be expressed as

$$\ln\left(\frac{1}{1 - y}\right) = kt^n$$

Now taking natural logarithms again, leads to

$$\ln\left[\ln\left(\frac{1}{1 - y}\right)\right] = \ln k + n \ln t$$

which is the form of the equation that we will now use. From the 150°C curve of Figure 15.17, let us arbitrarily choose two percent crystallized values of 20% and 80% (i.e., $y_1 = 0.20$ and $y_2 = 0.80$). The corresponding time values are $t_1 = 220$ min and $t_2 = 460$ min (realizing that the time axis is scaled logarithmically). Thus, our two simultaneous equations become

$$\ln\left[\ln\left(\frac{1}{1 - 0.20}\right)\right] = \ln k + n \ln (220)$$

$$\ln\left[\ln\left(\frac{1}{1-0.80}\right)\right] = \ln k + n \ln (460)$$

from which we obtain the values $n = 2.68$ and $k = 1.2 \times 10^{-7}$.

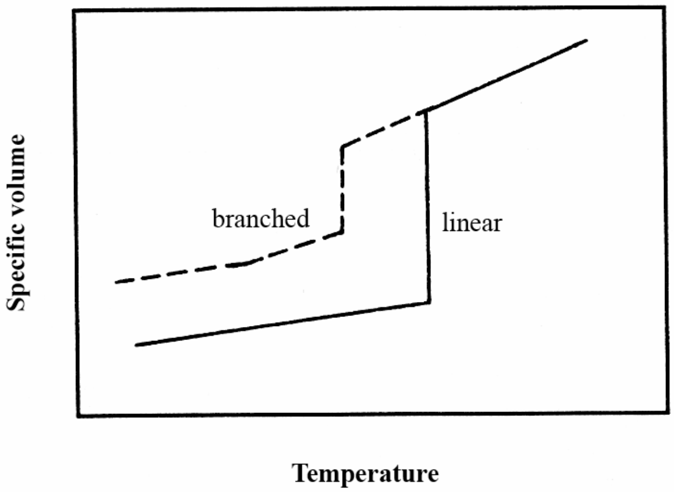
Melting and Glass Transition Temperatures

15.28 This question asks us to name which, of several polymers, would be suitable for the fabrication of cups to contain hot coffee. At its glass transition temperature, an amorphous polymer begins to soften. The maximum temperature of hot coffee is probably slightly below 100°C (212°F). Of the polymers listed, only polystyrene and polycarbonate have glass transition temperatures of 100°C or above (Table 15.2), and would be suitable for this application.

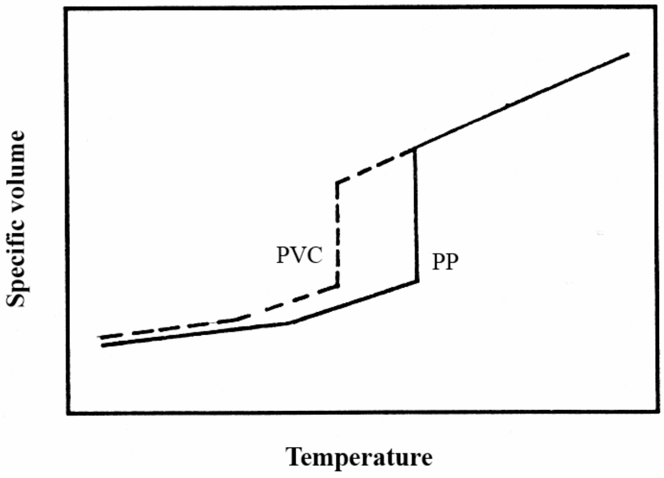
15.29 In order for a polymer to be suited for use as an ice cube tray it must have a glass-transition temperature below 0°C. Of those polymers listed in Table 15.2 only low-density and high-density polyethylene, PTFE, and polypropylene satisfy this criterion.

Factors That Influence Melting and Glass Transition Temperatures

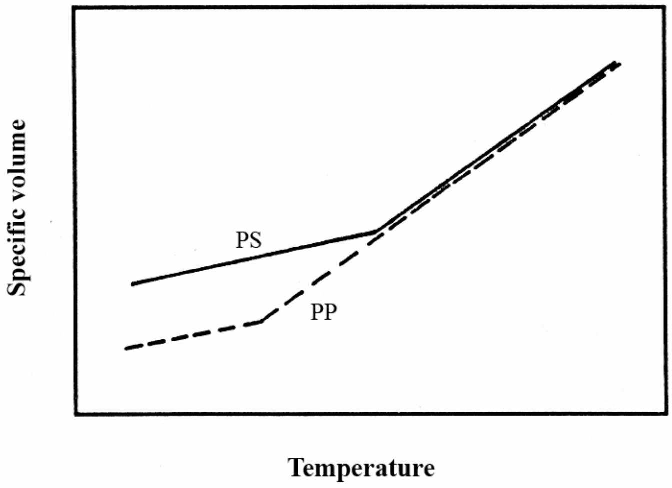
15.30 (a) Shown below are specific volume-versus-temperature curves for the two polyethylene materials. The linear polyethylene will be highly crystalline, and, therefore, will exhibit behavior similar to curve *C* in Figure 15.18. The branched polyethylene will be semicrystalline, and, therefore its curve will appear as curve *B* in this same figure. Furthermore, since the linear polyethylene has the greater molecular weight, it will also have the higher melting temperature.



(b) Shown below are specific volume-versus-temperature curves for the poly(vinyl chloride) and polypropylene materials. Since both are 50% crystalline, they will exhibit behavior similar to curve *B* in Figure 15.18. However, since the polypropylene has the greater molecular weight it will have the higher melting temperature. Furthermore, polypropylene will also have the higher glass-transition temperature inasmuch as its CH_3 side group is bulkier than the Cl for PVC.



(c) Shown below are specific volume-versus-temperature curves for the polystyrene and polypropylene materials. Since both are totally amorphous, they will exhibit the behavior similar to curve *A* in Figure 15.18. However, since the polystyrene repeat unit has a bulkier side group than polypropylene (Table 14.3), its chain flexibility will be lower, and, thus, its glass-transition temperature will be higher.



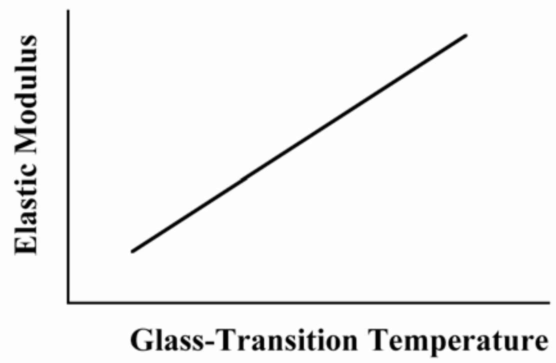
15.31 (a) Yes, it is possible to determine which polymer has the higher melting temperature. The linear polyethylene will most likely have a higher percent crystallinity, and, therefore, a higher melting temperature than the branched polyethylene. The molecular weights of both materials are the same and, thus, molecular weight is not a consideration.

(b) Yes, it is possible to determine which polymer has the higher melting temperature. Of these two polytetrafluoroethylene polymers, the PTFE with the higher density (2.20 g/cm^3) will have the higher percent crystallinity, and, therefore, a higher melting temperature than the lower density PTFE. The molecular weights of both materials are the same and, thus, molecular weight is not a consideration.

(c) Yes, it is possible to determine which polymer has the higher melting temperature. The linear polyethylene will have the greater melting temperature inasmuch as it will have a higher degree of crystallinity; polymers having a syndiotactic structure do not crystallize as easily as those polymers having identical single-atom side groups. With regard to molecular weight, or rather, degree of polymerization, it is about the same for both materials (8000), and therefore, is not a consideration.

(d) No, it is not possible to determine which of the two polymers has the higher melting temperature. The syndiotactic polypropylene will have a higher degree of crystallinity than the atactic material. On the basis of this effect alone, the syndiotactic PP should have the greater T_m, since melting temperature increases with degree of crystallinity. However, the molecular weight for the syndiotactic polypropylene (500,000 g/mol) is less than for the atactic material (750,000 g/mol); and this factor leads to a lowering of the melting temperature

15.32 For an amorphous polymer, the elastic modulus may be enhanced by increasing the number of crosslinks (while maintaining the molecular weight constant); this will also enhance the glass transition temperature. Thus, the modulus-glass transition temperature behavior would appear as



Elastomers

Fibers

Miscellaneous Applications

15.33 The backbone chain of most polymers consists of carbon atoms that are linked together. For the silicone polymers, this backbone chain is composed of silicon and oxygen atoms that alternate positions.

15.34 Two important characteristics for polymers that are to be used in fiber applications are: (1) they must have high molecular weights, and (2) they must have chain configurations/structures that will allow for a high degrees of crystallinity.

15.35 Five important characteristics for polymers that are to be used in thin-film applications are: (1) low density; (2) high flexibility; (3) high tensile and tear strengths; (4) resistance to moisture/chemical attack; and (5) low gas permeability.

Polymerization

15.36 For addition polymerization, the reactant species have the same chemical composition as the monomer species in the molecular chain. This is not the case for condensation polymerization, wherein there is a chemical reaction between two or more monomer species, producing the repeating unit. There is often a low molecular weight by-product for condensation polymerization; such is not found for addition polymerization.

15.37 (a) This problem asks that we determine how much ethylene glycol must be added to 20.0 kg of terephthalic acid to produce a linear chain structure of poly(ethylene terephthalate) according to Equation 15.9. Since the chemical formulas are provided in this equation we may calculate the molecular weights of each of these materials as follows:

$$MW(\text{ethylene glycol}) = 2(A_\text{C}) + 6(A_\text{H}) + 2(A_\text{O})$$

$$= 2(12.01 \text{ g/mol}) + 6(1.008 \text{ g/mol}) + 2(16.00 \text{ g/mol}) = 62.07 \text{ g/mol}$$

$$MW(\text{terephthalic acid}) = 8(A_\text{C}) + 6(A_\text{H}) + 4(A_\text{O})$$

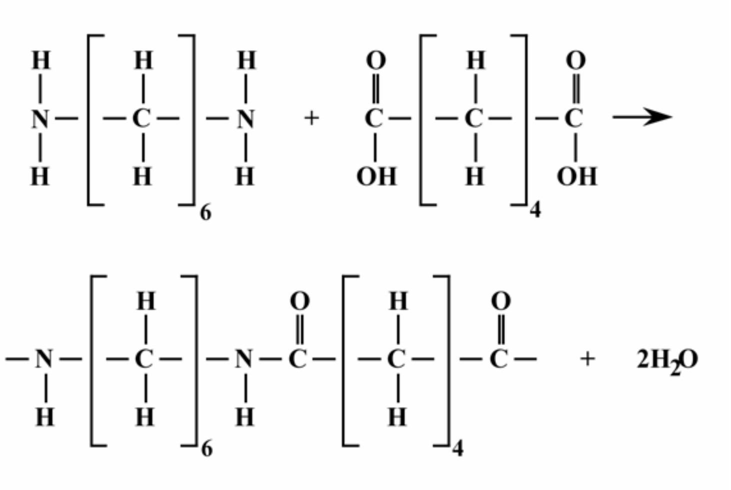
$$= 8\,(12.01 \text{ g/mol}) + 6(1.008 \text{ g/mol}) + 4(16.00 \text{ g/mol}) = 166.13 \text{ g/mol}$$

The 20.0 kg mass of terephthalic acid equals 20,000 g or $\dfrac{20{,}000\text{ g}}{166.13\text{ g/mol}} = 120.39$ mol. Since, according to Equation 15.9, each mole of terephthalic acid used requires one mole of ethylene glycol, which is equivalent to (120.39 mol)(62.07 g/mol) = 7473 g = 7.473 kg.

(b) Now we are asked for the mass of the resulting polymer. Inasmuch as one mole of water is given off for every repeat unit produced, this corresponds to 120.39 moles or (120.39 mol)(18.02 g/mol) = 2169 g or 2.169 kg since the molecular weight of water is 18.02 g/mol. The mass of poly(ethylene terephthalate) is just the sum of the masses of the two reactant materials [as computed in part (a)] minus the mass of water released, or

$$\text{mass [poly(ethylene terephthalate)]} = 20.0 \text{ kg} + 7.473 \text{ kg} - 2.169 \text{ kg} = 25.304 \text{ kg}$$

15.38 This problem asks for us to calculate the masses of hexamethylene diamine and adipic acid necessary to yield 20 kg of completely linear nylon 6,6. The chemical equation for this reaction is the answer to Concept Check 15.12, which is as follows:



From this equation we may calculate the molecular weights of these molecules.

$$MW(\text{adipic}) = 6(A_C) + 10(A_H) + 4(A_O)$$

$$= 6(12.01\text{ g/mol}) + 10(1.008\text{ g/mol}) + 4(16.00\text{ g/mol}) = 146.14\text{ g/mol}$$

$$MW(\text{hexamethylene}) = 6(A_C) + 16(A_H) + 2(A_N)$$

$$= 6(12.01\text{ g/mol}) + 16(1.008\text{ g/mol}) + 2(14.01\text{ g/mol}) = 116.21\text{ g/mol}$$

$$MW(\text{nylon}) = 12(A_C) + 22(A_H) + 2(A_N) + 2(A_O)$$

$$= 12(12.01\text{ g/mol}) + 22(1.008\text{ g/mol}) + 2(14.01\text{ g/mol}) + 2(16.00\text{ g/mol})$$

$$= 226.32\text{ g/mol}$$

The mass of 20 kg of nylon 6,6 equals 20,000 g or

$$m(\text{nylon}) = \frac{20{,}000 \text{ g}}{226.32 \text{ g/mol}} = 88.37 \text{ mol}$$

Since, according to the chemical equation given above, each mole of nylon 6,6 that is produced requires one mole each of adipic acid and hexamethylene diamine, with two moles of water as the by-product. The masses corresponding to 88.37 moles of adipic acid and hexamethylene diamine are as follows:

$$m(\text{adipic}) = (88.37 \text{ mol})(146.14 \text{ g/mol}) = 12{,}914 \text{ g} = 12.914 \text{ kg}$$

$$m(\text{hexamethylene}) = (88.37 \text{ mol})(116.21 \text{ g/mol}) = 10{,}269 \text{ g} = 10.269 \text{ kg}$$

Polymer Additives

15.39 The distinction between dye and pigment colorants is that a dye dissolves within and becomes a part of the polymer structure, whereas a pigment does not dissolve, but remains as a separate phase.

Forming Techniques for Plastics

15.40 Four factors that determine what fabrication technique is used to form polymeric materials are: (1) whether the polymer is thermoplastic or thermosetting; (2) if thermoplastic, the softening temperature; (3) atmospheric stability; and (4) the geometry and size of the finished product.

15.41 This question requests that we compare polymer molding techniques. For compression molding, both heat and pressure are applied after the polymer and necessary additives are situated between the mold members. For transfer molding, the solid materials (normally thermosetting in nature) are first melted in the transfer chamber prior to being forced into the die. And, for injection molding (normally used for thermoplastic materials), the raw materials are impelled by a ram through a heating chamber, and finally into the die cavity.

Fabrication of Fibers and Films

15.42 Fiber materials that are melt spun must be thermoplastic because: (1) In order to be melt spun, they must be capable of forming a viscous liquid when heated, which is not possible for thermosets. (2) During drawing, mechanical elongation must be possible; inasmuch as thermosetting materials are, in general, hard and relatively brittle, they are not easily elongated.

15.43 Of the two polymers cited, the one that was formed by extrusion and then rolled would have the higher strength. Both blown and extruded materials would have roughly comparable strengths; however the rolling operation would further serve to enhance the strength of the extruded material.

DESIGN QUESTIONS

15.D1 (a) Several advantages of using transparent polymeric materials for eyeglass lenses are: they have relatively low densities, and, therefore, are light in weight; they are relatively easy to grind to have the desired contours; they are less likely to shatter than are glass lenses; wraparound lenses for protection during sports activities are possible; and they filter out more ultraviolet radiation than do glass lenses.

The principal disadvantage of these types of lenses is that some are relatively soft and are easily scratched (although antiscratch coatings may be applied). Plastic lenses are not as mechanically stable as glass, and, therefore, are not as precise optically.

(b) Some of the properties that are important for polymer lens materials are: they should be relatively hard in order to resist scratching; they must be impact resistant; they should be shatter resistant; they must have a relatively high index of refraction such that thin lenses may be ground for very nearsighted people; and they should absorb significant proportions of all types of ultraviolet radiation, which radiation can do damage to the eye tissues.

(c) Of those polymers discussed in this chapter and Chapter 4, likely lens candidates are polystyrene, poly(methyl methacrylate), and polycarbonate; these three materials are not easily crystallized, and, therefore, are normally transparent. Upon consultation of their fracture toughnesses (Table B.5 in Appendix B), polycarbonate is the most superior of the three.

Commercially, the two plastic lens materials of choice are polycarbonate and allyl diglycol carbonate (having the trade name CR-39). Polycarbonate is very impact resistant, but not as hard as CR-39. Furthermore, PC comes in both normal and high refractive-index grades.

15.D2 There are three primary requirements for polymeric materials that are utilized in the packaging of food products and drinks; these are: (1) sufficient strength, to include tensile, tear, and impact strengths; (2) barrier protection--that is, being resistant to permeation by oxygen, water vapor, and carbon dioxide; and (3) being nonreactive with the food/drink contents--such reactions can compromise the integrity of the packaging material, or they can produce toxic by-products.

With regard to strength, poly(ethylene terephthalate) (PET or PETE) and oriented polypropylene (OPP) have high tensile strengths, linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE) have high tear strengths, while those polymers having the best impact strengths are PET and poly(vinyl chloride) (PVC). Relative to barrier characteristics, ethylene vinyl alcohol (EVOH) and poly(vinylidene chloride) (PVDC) copolymers are relatively impermeable to oxygen and carbon dioxide, whereas high-density polyethylene (HDPE), PVDC, polypropylene, and LDPE are impervious to water vapor.

Most common polymers are relatively nonreactive with food products, and are considered safe; exceptions are acrylonitrile and plasticizers used in PVC materials.

The aesthetics of packaging polymers are also important in the marketing of food and drink products. Some will be colored, many are adorned with printing, others need to be transparent and clear, and many need to be resistant to scuffing.

On the basis of the preceding discussion, examples of polymers that are used for specific applications are as follows:

PET(E) for soda pop containers;
PVC for beer containers;
LDPE and HDPE films for packaging bread and bakery products.

15.D3 The primary reasons that the automotive industry has replaced metallic automobile components with polymer and composite materials are: polymers/composites (1) have lower densities, and afford higher fuel efficiencies; (2) may be produced at lower costs but with comparable mechanical characteristics; (3) are in many environments more corrosion resistant; (4) reduce noise, and (5) are thermally insulating and thus reduce the transference of heat.

These replacements are many and varied. Several are as follows:

Bumper fascia are molded from an elastomer-modified polypropylene.

Overhead consoles are made of poly(phenylene oxide) and recycled polycarbonate.

Rocker arm covers are injection molded of a glass- and mineral-reinforced nylon 6,6 composite.

Torque converter reactors, water outlets, pulleys, and brake pistons, are made from phenolic thermoset composites that are reinforced with glass fibers.

Air intake manifolds are made of a glass-reinforced nylon 6,6.